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Applications of Successive Ionic Layer Adsorption and Reaction (SILAR) Technique for CZTS Thin Film Solar Cells

S. Sakthivel and V. Baskaran

Thin film Physics and Nano Science Laboratory,
PG and Research Department of Physics,
Rajah Serfoji Govt., College (Autonomous), Thanjavur, Tamilnadu, INDIA.
email: sakthivel.sunmugam@yahoo,com; bass.physikz@yahoo.com

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ABSTRACT

Use of successive ionic layer adsorption and reaction (SILAR) method was applied for the deposition of CZTS thin films at room temperature. Further, these films were immersed in anionic and cationic solutions at different number of cycles for structural improvement and characterized for structural, surface morphological, optical and electrical properties. Polycrystalline structure of CZTS was retained even after deposition as confirmed from XRD studies. The morphology of the film was examined by using scanning electron microscopy. The surface morphology of the CZTS thin films strongly depends on preparation route and deposition technique. The optical characteristics of the samples were obtained by using UV-Visible spectrophotometer at 200–900 nm wavelengths. The optical constants (refractive index, extinction coefficient etc.) of the CZTS thin films depend on preparation conditions.

Key words: SILAR, CZTS, Copper Chloride, Thioacetamide, $ZnSo_4$.

1. INTRODUCTION

Recently, CZTS thin films have attracted the more attention of researchers due to their optical and electrical properties. The optical spectra of CZTS films exhibit high transmission in the visible region and absorption throughout the near-infrared

region (800-1500 nm). The Cu2ZnSnS4 (CZTS) absorber has drawn an increasing amount of attention within thin-film solar cell technology owing to its optimal single-junction band gap (~1.5 eV) and high absorption coefficient (>10^4 cm^{-1}), in which the expensive group-III elements are substituted by group-II-IV elements, thereby forming the I_2–II–IV–VI_4 quaternary compound $Cu_2ZnSnSe_4$ (CZTSe) and its sulfide counterpart Cu_2ZnSnS_4 (CZTS). The band-gap energy Eg of the CIGSe alloy can be tuned from 1.04 to 1.68 eV and the gap energies of CZTS and CZTSe are around 1.0–1.5 eV, which is suitable for photovoltaic applications. Moreover, knowledge of the optical properties, such as the optical absorption coefficient, is required to analyze optical measurements as well as to optimize the solar cell devices. CZTS has been regarded as one of the most promising materials for light- harvesting materials in solar cells[1-4].

Power conversion efficiencies as high as 6.77% have been obtained using solar cells based on CZTS under AM1.5G illumination by Katagiri and co-workers. How- ever, theoretical limit for CZTS is reported to be 32.2%. Various other methods have also been employed to prepare CZTS thin films including electron beam evaporation[5], pulsed laser deposition (PLD)[6], electrodeposition[7], etc., a successive ionic layer adsorption and reaction (SILAR) method is one of the chemical methods for making uniform and large area thin films, which is based on immersion of the substrate into separately placed cations and anions. A simple solution based SILAR method has not yet been employed to synthesize a technologically important CZTS material.

The main goal of the present work is to deposit CZTS thin films by successive ionic layer adsorption and reaction (SILAR) method for photovoltaic applications.

2. EXPERIMENTAL

To fabricate CZTS thin films on cleaned glass substrates. CZTS thin films were deposited using 0.1M $CuCl_2$, 0.05M $ZnSo_4$, and 0.05M $SnCl_2$ for cationic solutions. The anionic solution was freshly prepared thioacetamide (C_2H_5S) for these films. The cationic and anionic precursor solutions characteristics: adsorption, reaction and rinsing times were detailed in literature for these thin films[7–9]. One SILAR cycle contained four steps: (a) the substrate was immersed into first reaction containing the aqueous cation precursor, (b) rinsed with water, (c) immersed into the anion solution, and (d) rinsed with water. The experiment was carried out at 120 SILAR cycles so that varied thickness was obtained. The substrates were first cleaned using distilled water and later dried in air. Figure 1 shows the scheme of SILAR technique for the deposition of CZTS thin films.

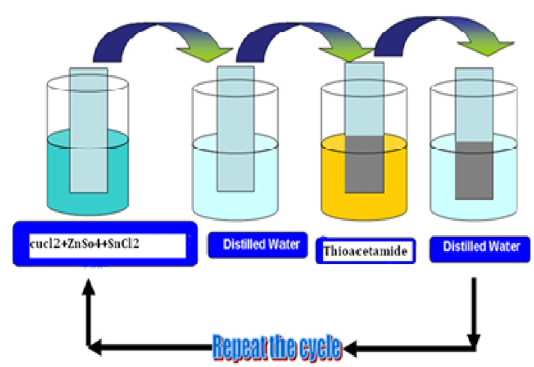

Fig. 1. Schematic representation of successive ionic layer adsorption and reaction (SILAR) method

3. RESULTS AND DISCUSSION

3.1. XRD analysis

The structural analysis of CZTS thin films was carried out by using X-ray diffractometer. The X-ray diffraction patterns of the CZTS thin films, grown at different SILAR cycles on glass substrates are shown in Figure 1.The XRD analysis shows that the thin films are kesterite phase CZTS with lattice parameters a = 4.8928Å and c = 10.536Å which is almost in agreement with the standard data. There is no difference among the XRD patterns of the nano-materials. The planes are oriented in the direction (110) and (202). The films exhibit tetragonal crystal structure.

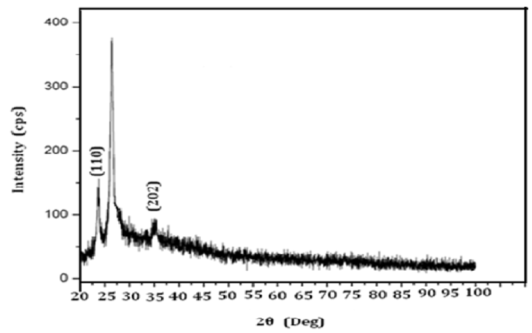

Fig.2 XRD pattern spectrum of the Cu_2ZnSnS_4 film

The highest intensity peak corresponds to (110) preferred orientation. The (110) peak is stronger than other peaks.

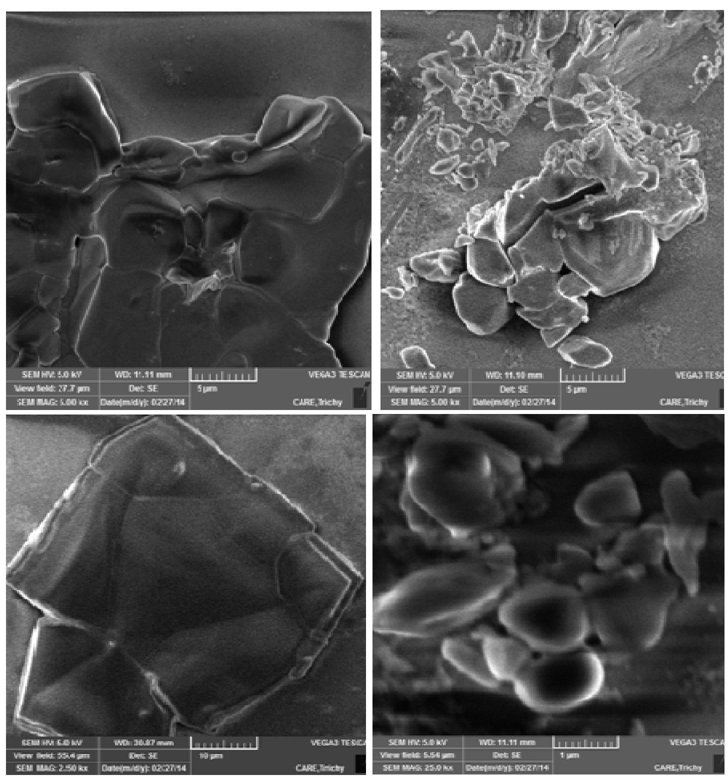

Figure 3: The SEM images of the CZTS thin film (a) 5 µm (b) 5 µm (c) 10 µm (d) 1 µm

3.2 Morphological analysis

Figure 2(a-d) shows the SEM micrograph of CZTS thin film. The formation of sub-micrometer crystallites distributed more or less uniformly over the surface is evident from the figure. Some holes indicating porosity and agglomeration of small crystallites also seem to be present in certain regions on the film surface. The size of crystallites are from 75nm to 840nm.

3.3 Optical Properties

The measured absorbance (A) of the film is related to transmittance (T) by

$$A = \log (1/T) = (I_0/I) \quad (1)$$

Where 'I' is the transmitted light and 'Io 'is the incident light. The absorption spectra of CZTS thin films measured as a function of wavelength of incident photons for different thicknesses. Absorption spectra of the film decreases at lower thickness and then increases for higher thickness film. The absorption edge increases with increase in thickness, except at higher thickness sample. Hence the film prepared at higher thickness exhibit lower conduction due to higher absorption behavior of the material. The absorption coefficient (α) is related to band gap (Eg) by

$$\alpha h\nu = (h\nu\text{-}Eg)^2 \text{ for indirect transition} \quad (2)$$

Where, 'ν' is the frequency of the incident light and 'h' is the Planck's constant. Band gap of the material can be determined from the plot of absorption coefficient vs. photon energy curve. Extrapolating the straight line portion of the plot of $(\alpha h\nu)^2$ against hν to the energy axis for zero absorption coefficients, the indirect band gap of CZTS material is determined. It is inferred that band gap decreases with increase in film thickness which may be due to change in the barrier height of the crystalline film.

4. CONCLUSIONS

Cu_2ZnSnS_4 thin films have been prepared on glass substrates by SILAR method using metallic precursor solutions followed by a four step cyclic approach. As deposited thin film has polycrystalline kesterite CZTS after completion of 120 SILAR cycles. Relatively sharper and intense peaks with increase in grain size are observed after deposition. XRD analysis of sample confirms the formation of CZTS compound but with some binary and tertiary compounds. Morphological study shows a compact film but with voids at some places. UV-VIS analysis of these film shows that band gap decreases with increase in film thickness which may be due to change in the barrier height of the crystalline film. Hence the film prepared at higher thickness exhibit lower conduction due to higher absorption behavior of the material. Based on the results of the analysis, it is concluded that CZTS with suitable physical properties can be fabricated for solar cell by SILAR method.

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